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Synthesis and Mesomorphic Properties of New Liquid Crystalline Dimesogens

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Syntheses and mesomorphic properties of dimesogens incorporating dissimilar mesogenic units viz. cholesterol and substituted biphenyls are reported.

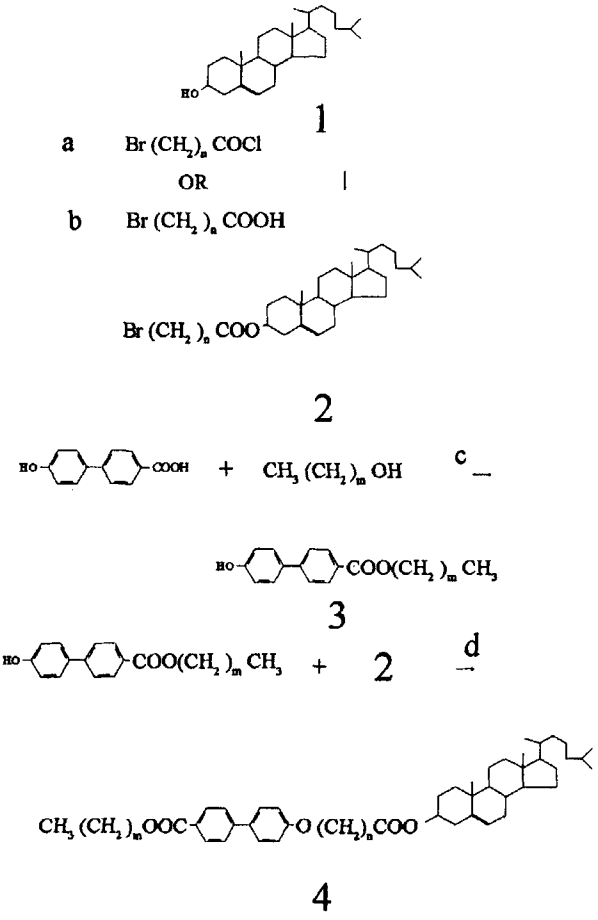
Keywords: dimesogens; synthesis

INTRODUCTION

Liquid crystalline dimers and oligomers are being investigated [1-5] in recent years as they are intermediates between low molecular mass liquid crystals and liquid crystalline polymer. The interest in mesogenic dimers stems not only from their ability to act as model compounds for liquid crystalline polymers but also from their quite different properties to conventional low mass liquid crystals. Liquid crystalline dimesogens which comprise of two mesogenic units, dissimilar in their chemical nature, are also being studied to study the effect of dissimilarity on the mesophase behavior of dimers. Recently Hardouin et. al.[6] reported the synthesis and mesomorphic properties of dimesogenic materials which exhibit interesting incommensurate smectic phases. Incommensurate smectic-A phase has been reported [7-9] in binary mixtures of polar compounds and the existence of such a phase has been questioned [10-12]. The high-resolution x-ray diffraction study [10] of the incommensurate smectic-A phase in a mixture of DB_7OCN and 8OCB has shown that it is in fact a coexistence of two smectic-A phases. In view of these observations, the materials reported by Hardouin et.al.[6] are significant, but the materials are moisture sensitive Schiff's bases, and their investigations require dry experimental conditions. The dimesogens reported here are chemically stable and have the structural requirements to exhibit incommensurate smectic phases.

SYNTHESIS

The liquid crystalline dimesogens were synthesized following the reaction sequence shown in scheme 1.



a) Pyridine, DMF b) Ligroin, PTS c) Toluene, H^+ d) Acetone, K_2CO_3

Scheme 1

Cholesterol was esterified with *w*-bromoacid chloride in presence of pyridine to give the *w*-bromoalkylcarbonyloxycholesterol. Esterification of cholesterol to obtain *w*-bromoalkycarbonyloxycholesterol was also performed using *w*-bromocarboxylic acid and *p*-toluenesulfonic acid in ligroin[13]. The final dimesogens were obtained by reacting *w*-bromoalkylcarbonyloxycholesterol with n-alkyl 4'-hydroxybiphenyl-4-carboxylate in presence of potassium carbonate in dry acetone. All the compounds were purified by flash chromatography and crystallization until they showed a single spot on TLC . The synthesis of n-pentyl 4'-[(6-cholesteryloxycarbonyl)pentyloxy]-biphenyl-4-carboxylate is described in detail.

PROPERTIES

The phase transition temperatures of the dimesogens are given in table 1. The isotropic to cholesteric and the cholesteric to smectic phase transition enthalphies are also given in the table. The length of the spacer in terminally attached dimers significantly modify the phase transition temperature and the same is seen in the dimesogens reported here. The cholesteric to isotropic phase transition temperature decreases as the spacer length increases and it significant for the dimesogens with spacer length of ten methylene units. The cholesteric to smectic phase transition also decreases as the spacer length increases. It is also seen that the length of the substituent on the biphenyl moiety also affects the phase transition temperatures and melting transition. The dimesogens #4 on cooling from the isotropic liquid resulted in the cholesteric phase in the form of cholesteric fan defects which changed to S_a phase around 154^0. The material showed a phase transition aruond 145^0 as seen by DSC but with little texture change.

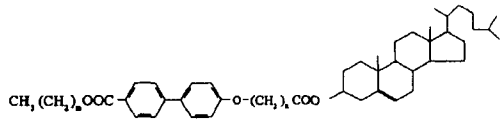
CONCLUSION

The synthesis and mesomorphic properties of dimesogens incorporating dissimilar mesogenic units are reported. All the dimesogens showed cholesteric and smectic phase. These materials are being investigated in detail by high resolution x-ray crystallography.

EXPERIMENTAL

6-Bromohexanoyl chloride and *w*-bromo n-alkanoic acids were purchased from Aldrich Chemical Co. TLC data were collected from Anal-Tech silica gel GHLF Uniplates and UV light or iodine vapor as detectors. Flash chromatography was done on E.Merck silica gel (200-400 mesh) under nitrogen (10-15 psi).

Table 1
Transition temperatures (°) for:



#	*m*	*n*	K	S_x	S_e	S_c	S_a	Ch	I
1	3	5	•110.0	_	_	_	•162.8 [2.10]	•178.2 [2.55]	•
2	3	7	•86.70	_	_	_	•155.8 [3.33]	•159.7 [2.68]	•
3	3	10	•82.00	_	_	_	•120.4 [2.00]	•127.4 [1.66]	•
4	4	5	•118.0	-	_	-	•154.5 [0.13]	•174.5 [2.24].	•
5	4	7	•121.9	_	_	_	•151.2 [3.29]	•158.9 [3.29]	•
6	4	10	•98.40	_	_	_	•117.7 [2.31]	•126.2 [1.71]	•
7	5	5	•132.0	(•99.0)	_	(•111)	•160.5 [1.47]	•166.7 [3.52]	•
8	5	7	•137.8	_	(•68.0)	_	•143.2 [2.64]	•151.8 [3.26]	•
9	5	10	•82.00	_	_	_	•111.7 [2.35]	•120.4 [1.74]	•

[ ])H Kj/mole, S_x-unidentified smectic

IR spectra were obtained using a Pye Unicam 3-200 instrument and NMR spectra were run in $CDCl_3$ with TMS as the internal standard using Varian Gemini 200 MHZ instrument. Microscopic observations were made using Nikon polarizing microscope fitted with a Mettler FP 82 HT hot stage and a Mettler FP 80 central processor. DSC scans were run using Perkin Elmer DSC 4 at a heating rate of 5^0 per minute.

Cholesteryl 6- bromohexanoate, *2*

A solution of cholesterol (2.44 g , 6.31 mmoles) , in tetrahydrofuran (10ml) and pyridine (0.5ml) was added dropwise with stirring to 6-bromohexanoyl chloride (1.49 g , 6.97 mmoles) and stirred at ambient temperature for 24 hr. The reaction mixture was added to distilled water (150 ml) and the precipitated solid was washed successively with water, 10% aqueous $NaHCO_3$ solution and water. Purification by flash chromatography on silica gel (CH_2Cl_2) gave the compound *2*. 2.42 g (67.6%), mp. 104-5, TLC (CH_2Cl_2) R_f= 0.76 , IR (nujol) , 1720, (ester C=O) , 1460, 1380, 1375, 1230, 1180, 1000, and 800 cm^{-1} and ^1H NMR ($CDCl_3$) δ 0.67-1.1 (15H, methyl groups of cholesterol), 1.1-2.0 (28H, complex multiplets, methylene and methine H of cholesterol), 2.4 (t, 2H, $-CH_2COO$), 3.4 (t, 2H, CH_2Br), 4.75(m, 1H, COOCH) and 5.4(d, 1H, C=C-H).

n-Pentyl 4'-hydroxybiphenyl-4-carboxylate, *3*

To 4'-hydroxy-4-biphenylcarboxylic acid (1.0 g, 4.76 mmoles), 1-pentanol (0.93 10.7 mmoles)in toluene (30 ml) , and concentrated sulfuric acid (0.05 mol) were added . The mixture was heated under reflux with a Dean-Stark water separator until all the acid went into solution , and then allowed to cool. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography using dichloromethane as the eluent. The material was further purified by crystallization using hexane/chloroform to give the white crystalline material *3*. 0.91 g, (74.7%), mp.104-5, TLC(CH_2Cl_2) R_f=0.32, IR (nujol), 3300.3250, (OH, phenolic), 1700(ester C=O),1580, 1480, 1280, 1120, 820 and 780 cm^{-1}.NMR ($CDCl_3$) δ 0.9 (t, 3H, $-CH_3$) 1.2-1.5 (b, m, 4H, methylene H), 1.8(m, 2H, $-CH_2-$) ,4.3(t, 2H, $COOCH_2$) ,5.7 (s,1H, phenolic H) , 6.9 (d,2, Ar H, ortho to OH) ,7.5-7.7 (m, 4H, Ar H,) , 8.05(d, ArH, ortho to ester).

n-Pentyl 4'-[(6-cholesteryloxycarbonyl)pentyloxy]-biphenyl-4-carboxylate, *4*

A mixture of cholesteryl-6-bromohexanoate (0.84 g, 1.49 mmoles), n-pentyl 4'-hydroxylbiphenyl 4-carboxylate(0.29 g, 0.97 mmoles), potassium carbonate(0.21 g, 1.5 mmoles), and potassium iodide(15 mg) in dry acetone (30 ml) was heated under reflux with stirring in an atmosphere of dry nitrogen for 48 hr. Acetone was

removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (30ml) and washed with water(2x15ml) and dried over anhydrous Na_2SO_4. The product obtained after evaporation of solvent was purified by flash chromatography using 1:1 mixture of hexane and methylene chloride as the eluent to give *4*. 0.41g (52.0%) TLC (CH_2Cl_2/hexane,1:1) R_f=0.2, IR (nujol) 1725 (ester C=O), 1725 (ester C=O), 1600, 1480, 1380, 1300, 1210, 1200, 1120, 840, and 780 cm^{-1}, NMR($CDCl_3$) δ 0.7-1.1 (15H, CH_3 of cholesterol), 1.1-2.0 (28H, complex multiplets, methylene and methine H of cholesterol), 2.4 (t, 2H, CH_2 COO), 4.0 (t ,2H, CH_2 COO), 4.3 (t, 2H,-$COOCH_2$) 4.75 (m, 1H, COOCH), 5.4 (d, 1H, C=CH), 6.95 (d, 2H, ArH), 7.56 (m, 4H, ArH), and 8.07 (d, 2H, ArH).

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